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(71)Applicant : SUMITOMO METAL MINING CO LTD

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(72)Inventor : TAMIYA YUKIHIRO
TAKENAKA MIKIMATA

(54) MANUFACTURE OF POLYIMIDE BASE PLATE

(57)Abstract:

PURPOSE: To obtain a method for preparation of a polyimide base plate which enables preparation of a printed wiring board of high reliability, a flexible printed circuit and an automatic bonding tape and which has a large strength of adhesion between an electroless plating film and an electrolytic plating film.

CONSTITUTION: In a manufacturing method of a polyimide base plate having a conductive film provided on one or both surfaces of polyimide resin, a conductive thin film of a thickness 10 μ m or below or preferably 5 μ m or below is provided on the surface of the polyimide resin and then subjected to heat treatment of 300 to 500° C in an inactive atmosphere. Subsequently, the surface of the conductive film is washed with a solution containing at least one kind of ions of hypochlorite, chlorite and perchlorate and then the surface of the conductive thin film is subjected further to electroplating, whereby the conductive film is formed.

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CLAIMS

[Claim(s)]

[Claim 1] In the manufacture approach of a polyimide substrate of having prepared the conductive film in one side of polyimide resin, or both sides After preparing a conductive thin film 10 micrometers or less in a polyimide resin front face, this is heat-treated at 300-500 degrees C in an inert atmosphere. The solution containing at least one sort of ion of a hypochlorite, chlorous-acid ion, and the perchloric acid ion washes the front face of this conductive film. Subsequently, subsequently The manufacture approach of the polyimide substrate characterized by forming a conductive film in the front face of this conductive thin film by giving electroplating further.

[Claim 2] The manufacture approach of the polyimide substrate according to claim 1 characterized by performing the postheat treatment which prepared the conductive thin film in one side of polyimide resin, or both sides by at least one approach in the sputtering method, vacuum deposition, the ion plating method, a nonelectrolytic plating method, the casting method, thermocompression bonding, and the electrolysis galvanizing method.

[Claim 3] The solution containing at least one sort in a hypochlorite, chlorous-acid ion, and perchloric acid ion is temperature, 10-60 degrees C, concentration The manufacture approach of claim 1 characterized by being a with 0.01-5 mols [l.] /and a pH of seven or more solution, and washing time amount being for [5 seconds -] 30 minutes thru/or a polyimide substrate given in dyadic.

[Claim 4] The manufacture approach of claim 1 characterized by a conductive thin film and a conductive film consisting of at least one sort in copper, gold, silver, nickel, cobalt, palladium, a conductive oxide, and a semi-conductor thru/or a polyimide substrate given in 3 terms.

[Claim 5] The manufacture approach of claim 1 characterized by said conductive film being 5 micrometers or less thru/or a polyimide substrate given in 4 terms.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the good polyimide substrate of the adhesion at the time of an elevated temperature.

[0002]

[Description of the Prior Art] Polyimide resin has the outstanding thermal resistance, and that of mechanical, electric, and chemical property is good, and is equal as compared with other plastics. For this reason, this polyimide resin is used as an insulating material of components for electrical machinery and apparatus, such as a printed wired board (PWB), a flexible printed circuit (FPC), and a substrate for tape-automated-bonding (TAB) mounting.

[0003] Such PWB, FPC, and the substrate for TAB mounting are formed by processing the substrate which prepared the conductive film in the polyimide resin front face. As an approach of forming a conductive film directly, the sputtering method, vacuum deposition, the ion plating method, a nonelectrolytic plating method, the casting method, thermocompression bonding, etc. are in polyimide resin. However, in the substrate formed by these approaches, when this substrate is left for 10 minutes under the hot environments of 200 degrees C, there is a fault of the adhesion reinforcement of a conductive film and polyimide resin falling remarkably, and it becoming impossible to use it. That this fault should be canceled, although various approaches are examined, and it is the most effective in them, the approach of heat-treating this substrate at the temperature of 200 degrees C or more is in one. According to this approach, surely, it is improved sharply and adhesion reinforcement under hot environments is carried out. However, in relation to the thickness of a conductive film, the more the thickness of a coat becomes thick, an improvement degree has the phenomenon in which a fall degree will become remarkable if it falls and thickness exceeds 10 micrometers, and the more this improvement degree has the trouble of producing the variation in adhesion reinforcement, between the products obtained.

[0004] Further examination is advanced that this trouble should be canceled and the approach of heat-treating, after performing nonelectrolytic plating to polyimide resin is examined. By this approach, it turned out that the adhesion reinforcement of a nonelectrolytic plating coat and polyimide resin becomes large, and the stable value is acquired. However, the postheat treatment was carried out and, subsequently to after activation, such as alkaline degreasing, electrolytic degreasing, and acid washing, it turned out [which were performed for the nonelectrolytic plating coat] that will be exfoliated in the front face of a nonelectrolytic plating coat more easily than the boundary of a nonelectrolytic plating coat and an electrolysis plating coat if an electrolysis plating coat is given. If PWB, FPC, and TAB are created using such a substrate, it will become the object which produces exfoliation and short-circuit of a lead, and an open circuit, and is unreliable.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is in offer of the creation approach of the nonelectrolytic plating coat and electrolysis plating coat which enable creation of PWB, FPC, and TAB which have high-reliability, and a polyimide substrate with large adhesion reinforcement.

[0006]

[Means for Solving the Problem] In the manufacture approach of a polyimide substrate that the approach of this invention which solves the above-mentioned technical problem prepared the conductive film in one side of polyimide resin, or both sides After preparing preferably 10 micrometers or less of conductive thin films 5 micrometers or less in a polyimide resin front face, This is heat-treated at 300-500 degrees C in an inert atmosphere, and, subsequently the solution containing at least one sort of ion of a hypochlorite, chlorous-acid ion, and the perchloric acid ion washes the front face of this conductive film. Subsequently It is characterized by forming a conductive film in the front face of this conductive thin film by giving electroplating further.

[0007]

[Function] Generally, when preparing an electrolysis plating coat on a conductive thin film, in order to remove surface dirt and the surface oxide film of a conductive thin film, activation, such as alkaline degreasing, electrolytic degreasing, and acid washing, is performed. This purpose is for preventing exfoliation with a conductive thin film and an electrolysis plating coat. When preparing an electrolysis plating coat on it after preparing a conductive thin film in a polyimide resin front face, by the object which did not heat-treat, but performed said activation and performed electrolysis plating, the adhesion reinforcement of a conductive thin film and an electrolysis plating coat is large, and exfoliation breaks out from the interface of a conductive thin film and polyimide resin. If the solution which exfoliation breaks out and contains at least one sort in a hypochlorite, chlorous-acid ion, and perchloric acid ion in activation from the interface of a conductive thin film and an electrolysis plating coat why when said pretreatment is performed is used, it is similarly [after heat-treating] and electrolysis plating is subsequently performed is used, it is not clear whether the adhesion reinforcement of a conductive thin film and an electrolysis plating coat becomes large. An object like the inorganic carbon which matter, such as non-polymerization matter and a plasticizer, volatilized, and was pyrolyzed and generated from polyimide resin during heat treatment adhered to the conductive thin film front face, and this invention persons have blocked activation on this front face of a thin film, and presume what will not become activable without an object with a strong oxidizing quality like a hypochlorite, chlorous-acid ion, and perchloric acid ion.

[0008] In this invention, in each, the solution containing a hypochlorite, chlorous-acid ion, and perchloric acid ion dissolves in water, and is not [perchlorate / a hypochlorite, chlorite, and] scrupulous about especially the class of each salt. For example, in the case of a hypochlorite, sodium salt and potassium salt are more suitable than a price and the ease of dealing with it. [0009] Since pretreatment conditions, such as concentration of each ion, are influenced by the heat treatment conditions of a nonelectrolytic plating coat, they cannot be limited, but in order to be usually by 1 in 0.01-5 mols / and to prevent disassembly of each ion, it is desirable to make pH or more into seven. Moreover, as for the processing time, for [5 seconds -] 30 minutes is desirable, and the solution temperature at the time of processing has 10-60 degrees C more desirable than the viewpoint of aggravation prevention of work environment.

[0010] The conductive thin film as used in the field of this invention and an electrolysis plating coat say the object obtained using metals, such as copper, gold, silver, nickel, cobalt, and palladium, these alloys, a conductive oxide, a semi-conductor, etc. This invention is further explained using an example below.

[0011]

[Example]

(Example 1) the Kaneka [CORP.] CORP. make with a magnitude of 30x30cm -- after immersing the test sample of the polyimide resin film of APIKARU NPI-50 for 30 seconds into 25-degree C 25% hydrazine hydrate solution and making a front face into a hydrophilic property, the mask of one side was carried out, the usual activation was performed, and nonelectrolytic plating processing was performed on the conditions shown below.

[0012] (Bath presentation)

CuSO4and5H2O 10 g/IEDTA and 2Na 30 g/(37%HCHO 5 g/l dipyrityl 20 mg/PEG#1000 0.5 g/l

[0013] (Plating conditions)

** Whenever 65 ** ** At the time of air stirring Between 20 Part [0014] The thickness of the obtained nonelectrolytic plating coat was 0.4 micrometers. This was put in all over the controlled atmosphere furnace, and the temperature up was carried out to 350 degrees C with 10-degree-C programming rate for /in argon atmosphere, and after heating at 350 degrees C for 10 hours, it cooled naturally to the room temperature, putting in a furnace. Then, electrolytic copper plating was performed on the conditions which are immersed for 3 minutes into a 25-degree C 3.5-mol [1.] sodium-hypochlorite solution, and show a copper front face subsequently to the following.

[0015] (Bath presentation)

CuSO4 and H2O 120 g/H2SO4 150 g/l [0016] (Electrolytic condition)

** Whenever 25 ** ** At the time of stirring by air blowing in Between 90 Current density between parts 2 The thickness of the coat of the copper obtained A/dm2 was 35 micrometers. [0017] Subsequently, the resist was applied to the copper front face, the predetermined mask was stuck, was exposed and developed, was etched, width of face of 10mm and a die-length 100mm band-like copper layer were formed, and adhesion was investigated by pulling up and tearing off the end of this copper layer in the direction of a right angle to a substrate.

Consequently, adhesion reinforcement is 1 kg/cm. A **** and exfoliation took place between the copper layer and the polyimide layer above, and it turned out that the adhesion of a nonelectrolytic plating coat and an electrolytic copper plating coat is good. Therefore, by using the polyimide substrate of this example shows that it is possible to create reliable PWB and reliable FPC, and TAB.

[0018] (Example 1 of a comparison) Except electrolytic degreasing having performed activation after heat treatment not using the sodium-hypochlorite solution, the substrate was obtained like the example 1 and the adhesion of a copper layer was investigated similarly. Consequently, adhesion reinforcement is 1 kg/cm. Dispersion and 23% of the total number of investigations had caused exfoliation between the nonelectrolytic plating coat and the electrolytic copper plating coat in order. This shows that neither reliable PWB and reliable FPC, nor TAB can be created with the substrate obtained by this approach.

[0019] (Example 2) The trial data which prepared the copper coat with a thickness of 0.6 micrometers by the spatter on the 30x30cm polyimide resin film of the Du Pont-Toray Kapton 200H mold of magnitude were paid all over the controlled atmosphere furnace, and after carrying out the temperature up and holding to 420 degrees C with 10-degree-C programming rate for /in argon atmosphere for 1 hour, it cooled naturally to the room temperature, putting in a furnace. Then, the copper front face was immersed for 10 seconds into the 25-degree C 3.1-mol [1.] ammonium-perchlorate solution, subsequently electrolytic copper plating was performed like the example 1, and thickness obtained the 35-micrometer copper coat.

[0020] Subsequently, the adhesion reinforcement of a copper layer and a polyimide layer was investigated like the example 1. Consequently, adhesion reinforcement is 1 kg/cm. A **** and exfoliation took place between the copper layer and the polyimide layer above, and it turned out that the adhesion of an electrolytic copper plating coat and the copper coat which deposited by the spatter is good. Therefore, it is possible by using the polyimide substrate of this example to create reliable PWB and reliable FPC, and TAB.

[0021] (Example 2 of a comparison) Except alkaline degreasing having performed activation after heat treatment not using the ammonium-perchlorate solution, the substrate was obtained like the example 2 and the adhesion of a copper layer was investigated similarly. Consequently, adhesion reinforcement is 1 kg/cm. Exfoliation was caused between the copper coats and electrolytic copper plating coats which dispersion and 18% of the total number of investigations formed by the spatter in order. This shows that neither reliable PWB and reliable FPC, nor TAB can be created with the substrate obtained by this approach.

[0022] (Example 3) YUP! REXX with a magnitude of 30x30cm by Ube Industries [Ltd.]. Ltd. - After immersing the test sample of the polyimide resin film of 50SS molds for 30 seconds into 25-degree C 25% hydrazine hydrate solution and making a front face into a hydrophilic property, the mask of one side was carried out, the usual activation was performed, and non-electrolyzed nickel and boron plating processing were performed on the conditions shown below.

[0023] (Bath presentation)

NaSO4.6H2O 30 g/IDMAB 5 g/l glycine 18 g/l apple acid 27 g/l aqueous ammonia (28%) 30 g/l

[0024] (Plating conditions)

** Whenever 70 ** ** At the time of air stirring Between 2 Part [0025] The thickness of the obtained nonelectrolytic plating coat was 0.2 micrometers. This was put in all over the controlled atmosphere furnace, and after carrying out the temperature up and holding for 5 minutes to 480 degrees C with 100-degree-C programming rate for /in argon atmosphere, it cooled to the room temperature at 20-degree-C a rate for /. Then, the copper front face was immersed for 10 minutes into the 25-degree C 0.1-mol [1.] calcium-hypochlorite solution, subsequently electrolytic copper plating was performed like the example 1, and thickness obtained the 35-micrometer conductive film.

[0026] Subsequently, the adhesion reinforcement of a conductive film and a polyimide layer was investigated like the example 1. Consequently, adhesion reinforcement is 1kg/cm2. A **** and exfoliation took place between the conductive film and the polyimide layer above, and it turned out that the adhesion of an electrolytic copper plating coat, and a non-electrolyzed nickel and boron coat is good. Therefore, it is possible by using the polyimide substrate of this example to create reliable PWB and reliable FPC, and TAB.

[0027]

[Effect of the Invention] According to the approach of this invention, the good substrate of the adhesion of a conductive layer and a polyimide layer can be manufactured. And reliable PWB and reliable FPC, and TAB can be created by using the polyimide substrate which carried out in this way and was obtained.

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(21)出願番号	特願平3-12558	(71)出願人	000183303 住友金属鉱山株式会社 東京都港区新橋 5 丁目11番 3 号
(22)出願日	平成 3 年(1991) 1 月11日	(72)発明者	田宮 幸広 愛媛県新居浜市八幡町 3 - 4 - 31
		(72)発明者	竹中 幹又 愛媛県新居浜市星越町12-12

(54)【発明の名称】 ポリイミド基板の製造方法

(57)【要約】

〔目的〕 高信頼性を有するPWBやFPCやTABの作成を可能とする、無電解めっき被膜と電解めっき被膜と密着強度の大きいポリイミド基板の作成方法の提供。

〔構成〕 ポリイミド樹脂の片面、あるいは両面に導電性被膜を設けたポリイミド基板の製造方法において、ポリイミド樹脂表面に10 μ m以下好ましくは5 μ m以下の導電性薄膜を設けた後、これを不活性雰囲気中で300 \sim 500 $^{\circ}$ Cで熱処理し、次いで該導電性被膜の表面を次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンの内の少なくとも1種のイオンを含む溶液で洗浄し、次いで、該導電性薄膜の表面にさらに電気めっきを施すことにより導電性被膜を形成する。

【特許請求の範囲】

【請求項1】 ポリイミド樹脂の片面、あるいは両面に導電性被膜を設けたポリイミド基板の製造方法において、ポリイミド樹脂表面に10 μ m以下の導電性薄膜を設けた後、これを不活性雰囲気中で300～500℃で熱処理し、次いで該導電性被膜の表面を次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンの内の少なくとも1種のイオンを含む溶液で洗浄し、次いで、該導電性薄膜の表面にさらに電気めっきを施すことにより導電性被膜を形成することを特徴とするポリイミド基板の製造方法。

【請求項2】 ポリイミド樹脂の片面、あるいは両面にスパッタリング法、蒸着法、イオンプレーティング法、無電解めっき法、キャスト法、熱圧着法、電解めっき法の内少なくとも一つの方法により導電性薄膜を設けた後熱処理をおこなうことを特徴とする請求項1記載のポリイミド基板の製造方法。

【請求項3】 次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンの内の少なくとも1種を含む溶液が、温度10～60℃、濃度0.01～5モル/l、pH7以上の溶液であり、洗浄時間が5秒～30分間であることを特徴とする請求項1ないし2項記載のポリイミド基板の製造方法。

【請求項4】 導電性薄膜および導電性被膜が銅、金、銀、ニッケル、コバルト、パラジウム、導電性酸化物、半導体の内の少なくとも1種からなることを特徴とする請求項1ないし3項記載のポリイミド基板の製造方法。

【請求項5】 前記導電性被膜が5 μ m以下であることを特徴とする請求項1ないし4項記載のポリイミド基板の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、高温時の密着性の良好なポリイミド基板の製造方法に関する。

【0002】

【従来の技術】ポリイミド樹脂は優れた耐熱性を有し、又機械的、電氣的、そして化学的特性も良好で、他のプラスチックと比較して遜色がない。このため、該ポリイミド樹脂は、例えばプリント配線板(PWB)、フレキシブルプリント回路(FPC)、テープ自動ボンディング(TAB)実装用基板等の電気機器用部品の絶縁材料として用いられている。

【0003】このようなPWB、FPC、TAB実装用基板は、ポリイミド樹脂表面に導電性被膜を設けた基板を加工することにより形成される。ポリイミド樹脂に導電性被膜を直接形成する方法としてはスパッタリング法、蒸着法、イオンプレーティング法、無電解めっき法、キャスト法、熱圧着法等がある。しかし、これらの方法で形成した基板では、該基板を200℃とい

った高温環境下に10分間放置すると導電性被膜とポリイミド樹脂との密着強度が著しく低下し、使用できなくなるといった欠点がある。この欠点を解消すべく、種々の方法が検討されているが、それらの中で最も効果的とされるものの一つに該基板を200℃以上の温度で熱処理する方法がある。この方法によれば、確かに高温環境下での密着強度は大幅に改善されされる。しかし、この改善度合いは導電性被膜の厚さに関連し、被膜の厚さが厚くなればなるほど改善度合いは低下し、膜厚が10 μ mを越えると低下度合いが顕著となるという現象があり、得られる製品間に密着強度のバラツキを生じるとい

う問題点がある。
【0004】この問題点を解消すべくさらなる検討が進められ、ポリイミド樹脂に無電解めっきを行った後に熱処理を行う方法が検討されている。この方法では無電解めっき被膜とポリイミド樹脂との密着強度は大きくなり、且つ安定した値が得られることがわかった。しかし、無電解めっき被膜を施した後熱処理し、次いで無電解めっき被膜の表面をアルカリ脱脂、電解脱脂、酸洗等の活性化処理後に電解めっき被膜を施すと、無電解めっき被膜と電解めっき被膜との境界より容易に剥離することがわかった。このような基板を用いてPWBやFPCやTABを作成すると、リードの剥離やショートや断線を生じ信頼性の無い物となる。

【0005】

【発明が解決しようとする課題】本発明の目的は、高信頼性を有するPWBやFPCやTABの作成を可能とする、無電解めっき被膜と電解めっき被膜と密着強度の大きいポリイミド基板の作成方法の提供にある。

【0006】

【課題を解決するための手段】上記課題を解決する本発明の方法は、ポリイミド樹脂の片面、あるいは両面に導電性被膜を設けたポリイミド基板の製造方法において、ポリイミド樹脂表面に10 μ m以下好ましくは5 μ m以下の導電性薄膜を設けた後、これを不活性雰囲気中で300～500℃で熱処理し、次いで該導電性被膜の表面を次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンの内の少なくとも1種のイオンを含む溶液で洗浄し、次いで、該導電性薄膜の表面にさらに電気めっきを施すことにより導電性被膜を形成することを特徴とするものである。

【0007】

【作用】一般に、導電性薄膜の上に電解めっき被膜を設ける場合、導電性薄膜の表面の汚れや酸化膜を除去するためにアルカリ脱脂や電解脱脂や酸洗等といった活性化処理をおこなっている。この目的は導電性薄膜と電解めっき被膜との剥離を防止するためである。ポリイミド樹脂表面に導電性薄膜を設けた後、その上に電解めっき被膜を設ける場合、熱処理をおこなわず前記活性化処理をおこない電解めっきを行った物では導電性薄膜と電解め

つき被膜との密着強度は大きく、剥離は導電性薄膜とポリイミド樹脂との境界面より起きる。熱処理をおこなった後同様に前記前処理をおこない、次いで電解めっきをおこなうとなぜ導電性薄膜と電解めっき被膜との境界面より剥離が起き、活性化処理に次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンの内の少なくとも1種を含む溶液を用いると導電性薄膜と電解めっき被膜との密着強度が大きくなるのかは明確ではない。本発明者らは熱処理中にポリイミド樹脂より未重合物質や可塑剤等の物質が揮発し、熱分解して生成した無機炭素のような物が導電性薄膜表面に付着して該薄膜表面の活性化を妨害しており、次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンのような強い酸化性をもつ物によって初めて活性化が可能となるものと推定している。

【0008】本発明において、次亜塩素酸イオン、亜塩素酸イオン、過塩素酸イオンを含む溶液は、それぞれを次亜塩素酸塩、亜塩素酸塩、過塩素酸塩を水に溶解したものであり、各塩の種類については特にこだわるものではない。例えば、次亜塩素酸塩の場合には、価格、取扱い易さよりナトリウム塩やカリウム塩が適当である。

【0009】各イオンの濃度等の前処理条件は無電解めっき被膜の熱処理条件に影響されるため限定出来ないが、通常0.01～5モル/lで有り、各イオンの分解を防止するためにpHを7以上とすることが好ましい。又、処理時間は5秒～30分間が好ましく、処理時の液温は作業環境を悪化防止の観点より10～60℃が好ましい。

【0010】本発明でいう導電性薄膜や電解めっき被膜は銅、金、銀、ニッケル、コバルト、パラジウムなどの金属およびこれらの合金、そして導電性酸化物や半導体等を用いて得た物をいう。以下実施例を用いて本発明をさらに説明する。

【0011】

【実施例】

(実施例1) 30×30cmの大きさの鐘淵化学(株)社製アピカルNPI-50のポリイミド樹脂フィルムの試験試料を25℃の2.5%抱水ヒドラジン溶液中に30秒間浸漬し、表面を親水性にした後、片面をマスクし、通常の活性化処理を施し、以下に示す条件で無電解めっき処理をおこなった。

【0012】(浴組成)

CuSO ₄ ・5H ₂ O	10	g/l
EDTA・2Na	30	g/l
37%HCHO	5	g/l
ジピリジル	20	mg/l
PEG#1000	0.5	g/l

【0013】(めっき条件)

温度	65	℃
攪拌	空気攪拌	
時間	20	分

【0014】得られた無電解めっき被膜の厚さは0.4μmであった。これを雰囲気調整炉中に入れ、アルゴン雰囲気中で10℃/分の昇温速度で350℃まで昇温し、350℃で10時間加熱した後、炉内に入れたまま室温まで自然冷却した。その後、銅表面を25℃の3.5モル/l次亜塩素酸ナトリウム溶液中に3分間浸漬し、次いで以下に示す条件で電解銅めっきをおこなった。

【0015】(浴組成)

CuSO ₄ ・5H ₂ O	120	g/l
H ₂ SO ₄	150	g/l

【0016】(電解条件)

温度	25	℃
攪拌	空気吹込みによる攪拌	
時間	90	分間
電流密度	2	A/dm ²

得られた銅の被膜の厚さは35μmであった。

【0017】次いで、銅表面にレジストを塗布し、所定のマスクを密着し、露光し、現像し、エッチングして幅10mm、長さ100mmの帯状の銅層を形成し、該銅層の一端を基板に対して直角方向に引上げ、引き剥がすことにより密着性を調べた。その結果、密着強度は1kg/cm以上あり、且つ剥離は銅層とポリイミド層との間で起こり、無電解めっき被膜と電解銅めっき被膜との密着性は良好であることがわかった。よって、本実施例のポリイミド基板を用いることにより信頼性の高いPWBやFPCやTABを作成することは可能であることがわかる。

【0018】(比較例1)熱処理後の活性化処理を次亜塩素酸ナトリウム溶液を用いず、電解脱脂でおこなった以外は実施例1と同様にして基板を得、同様にして銅層の密着性を調べた。その結果、密着強度は1Kg/cm前後でばらつき、かつ全調査数の2.3%が無電解めっき被膜と電解銅めっき被膜との間で剥離を起こしていた。このことは、本方法で得た基板では信頼性の高いPWBやFPCやTABを作成することはできないことを示している。

【0019】(実施例2)30×30cmの大きさの東レ・デュボン社製カプトン200H型のポリイミド樹脂フィルム上にスパッタ法により0.6μmの厚さの銅被膜を設けた試験資料を雰囲気調整炉中に入れ、アルゴン雰囲気中で10℃/分の昇温速度で420℃まで昇温し、1時間保持した後、炉内に入れたまま室温まで自然冷却した。その後、銅表面を25℃の3.1モル/l過塩素酸アンモニウム溶液中に10秒間浸漬し、次いで実施例1と同じようにして電解銅めっきをおこない厚さは35μmの銅被膜をえた。

【0020】次いで、実施例1と同様にして銅層とポリイミド層との密着強度を調べた。その結果、密着強度は1kg/cm以上あり、且つ剥離は銅層とポリイミド

層との間で起こり、電解銅めっき被膜とスパッタ法により析出した銅被膜との密着性は良好であることがわかった。よって、本実施例のポリイミド基板を用いることにより信頼性の高いPWBやFPCやTABを作成することは可能である。

【0021】(比較例2)熱処理後の活性化処理を過塩素酸アンモニウム溶液を用いず、アルカリ脱脂でおこなった以外は実施例2と同様にして基板を得、同様にして銅層の密着性を調べた。その結果、密着強度は1kg/cm前後ではらつき、かつ全調査数の18%がスパッタ法で形成した銅被膜と電解銅めっき被膜との間で剥離を起こしていた。このことは、本方法で得た基板では信頼性の高いPWBやFPCやTABを作成することはできないことを示している。

【0022】(実施例3)30×30cmの大きさの宇部興産(株)社製ユービレックス-50SS型のポリイミド樹脂フィルムの試験試料を25℃の2.5%抱水ヒドラジン溶液中に30秒間浸漬し、表面を親水性にした後、片面をマスクし、通常の活性化処理を施し、以下に示す条件で無電解ニッケル・ほう素めっき処理をおこな

った。

【0023】(浴組成)

NiSO ₄ ・6H ₂ O	30	g/l
DMAB	5	g/l
グリシン	18	g/l
りんご酸	27	g/l
アンモニア水(28%)	30	g/l

【0024】(めっき条件)

温度	70	℃
攪拌	空気攪拌	
時間	2	分

【0025】得られた無電解めっき被膜の厚さは0.2μmであった。これを雰囲気調整炉に入れ、アルゴン雰囲気中で100℃/分の昇温速度で480℃まで昇温し、5分間保持した後、20℃/分の割合で室温まで冷却した。その後、銅表面を25℃の0.1モル/l次亜塩素酸カルシウム溶液中に10分間浸漬し、次いで実施例1と同じようにして電解銅めっきをおこない厚さは35μmの導電性被膜をえた。

【0026】次いで、実施例1と同様にして導電性被膜とポリイミド層との密着強度を調べた。その結果、密着強度は1kg/cm²以上あり、且つ剥離は導電性被膜とポリイミド層との間で起こり、電解銅めっき被膜と無電解ニッケル・ほう素被膜との密着性は良好であることがわかった。よって、本実施例のポリイミド基板を用いることにより信頼性の高いPWBやFPCやTABを作成することは可能である。

【0027】

【発明の効果】本発明の方法によれば導電層とポリイミド層との密着性の良い基板を製造できる。そして、このようにして得たポリイミド基板を用いることにより信頼性の高いPWBやFPCやTABを作成することができる。